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Performance of Single Point Monitor in Measuring Ammonia and Hydrogen Sulfide Gases

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Summary and Implication

Performance of Single Point Monitors (SPMs) was evaluated for measuring aerial ammonia (NH_3) and hydrogen sulfide (H_2S) under laboratory and field conditions. Calibration gas or $\text{NH}_3/\text{H}_2\text{S}$ -laden air at various dew-point temperatures (t_{dp}) were introduced simultaneously to the SPMs under evaluation and a chemiluminescence NH_3 analyzer or a pulsed-fluorescence H_2S analyzer. Linear relationships were found between readings of the SPMs and those of the respective gas analyzer. Moisture in the air positively influenced the SPM readings. The SPM readings for H_2S measurement can be corrected to achieve 90% to 107% agreement with the analyzer readings. However, such corrections proved not as effective for NH_3 measurements (59% to 90% agreement). To improve quality of H_2S data obtained with SPMs, moisture content of the sample air should be concurrently measured and its effect on output readings compensated.

Introduction

Ammonia (NH_3) and hydrogen sulfide (H_2S) associated with animal feeding operations (AFOs) have received particular attention due to their health effects on humans. Single Point Monitors (SPMs) (Model 7100, Zellweger Analytics, Inc., Lincolnshire, Ill.) have been used to monitor NH_3 and H_2S levels in or around swine facilities. The SPM measures gas levels based on the rate of color change of a chemical cassette tape that reacts with the target gas. The color intensity change of the tape is sensed by a photocell whose output is then converted to analog output and digital display of the gas level. A "chem-key" on the SPM determines the type of gas monitored and sets the range span for the gas, and also adjusts measurement time and internal calibration according to a factory-set algorithm. The advantages of SPM include its relatively low cost (~\$7000), portability for field application, and ability to detect relatively low gas concentrations. The main drawbacks and concerns about validity of the data obtained with SPMs include their large uncertainty (20% to 25% per manufacturer's specification), susceptibility to measurement interference by moisture content in the sample air, and the inability to calibrate the units in the field or by the user. Nonetheless,

SPMs have been used by certain states for checking compliance of state air quality standards. SPM is an approved method for measuring ambient H_2S by the Minnesota Pollution Control Agency.

The objective of this study was to characterize operational performance of SPMs with regard to measurement uncertainty, repeatability, stability, moisture interference, and interchangeability in measuring aerial NH_3 and H_2S under laboratory and field conditions.

Materials and Methods

A laboratory evaluation and verification system was set up to evaluate 44 SPMs for the anticipated ranges of NH_3 and H_2S (fig. 1). The chem-keys for NH_3 evaluation had a range of 0 to 30 parts per million (ppm) by volume. In this range, SPMs update the display every 15 s. The range of chem-keys for H_2S evaluation was 0 to 90 parts per billion (ppb) by volume with an updating interval of 15 min. Amines and hydrides chemcassette tapes (part no. 700342 and 700300, respectively, Zellweger Analytics) were used to evaluate NH_3 and H_2S , respectively.



Figure 1. Lab setups for evaluation of SPM performance in measurement of H_2S and NH_3 .

Calibration gases at various known concentrations were simultaneously introduced to the SPMs and the respective gas analyzer via a gas distribution system. Dry ($t_{dp} = -8^{\circ}\text{F}$) H_2S calibration gas at nominal concentrations of 0, 10, 20, 40, 60, or 70 ppb was generated to test H_2S , whereas dry NH_3 calibration gas of 0, 5, 10, 15, 20, or 25 ppm was generated to test NH_3 . A temperature- and humidity-controlled room was instrumented to carry out the lab evaluation of target gases in humid air. Three dew-point temperatures (t_{dp} , 48°F , 55°F , or 61°F) at a dry-bulb temperature of 76°F and four concentration levels (0, 12, 35, or 70 ppb H_2S or 0, 5, 15, or 25 ppm NH_3), in a factorial arrangement, were chosen for testing each target gas. Two potential factors contribute to the discrepancy in measurement by the SPM and the analyzer, i.e., inherent resolution of the SPM and interference by moisture in sample air. The degree of moisture interference may depend on the gas level. Hence, functional relationships were used to relate the SPM output to the analyzer value for each gas.

Between six and ten SPMs were randomly selected to monitor NH_3 or H_2S gas at a poultry or swine production site. Air samples from the exhaust stream were introduced into a distribution manifold and monitored simultaneously by SPMs and the reference gas analyzer. Measurements by each SPM and by the respective analyzer were paired for comparison.

To evaluate stability of the SPMs, lab tests using H_2S calibration gas were conducted 8 months after the initial evaluation, during which majority of the SPM units were employed periodically in field monitoring with an accumulated usage of 3 to 4 weeks. Twenty-five SPMs were randomly selected and evaluated with dry H_2S calibration gas ($t_{dp} = -8^{\circ}\text{F}$) at nominal levels of 0, 10, 20, 40, 60, or 70 ppb. A new set of linear regression equations were developed for the 25 SPMs and compared with the original set of equations for each SPM.

Results and Discussion

Lab Evaluation - Hydrogen Sulfide

Means and standard deviations (S.D.) of H_2S readings by the SPMs and the pulsed-fluorescence analyzer under dry air and humid air condition are shown in table 1. The within-units S.D. column shows variation among three consecutive updates of the SPMs, whereas the among-units S.D. column reflects variability or interchangeability among the units. The three consecutive updates by the same SPM for a given calibration gas level varied up to 6 ppb (up to 16% of the SPM reading) at relatively high concentrations (60 ppb). This result indicates a rather poor repeatability of the SPMs.

Comparisons in H_2S readings by the SPMs and the pulsed-fluorescence analyzer at the tested t_{dp} are shown in figure 2. Generally, SPM readings were lower for all the tested concentrations except for the dry zero air. However, the SPM readings increased with increasing

moisture content. Under laboratory conditions with t_{dp} of -8°F , 48°F , 55°F , or 61°F , the result of using SPMs to measure the change in H_2S concentration will be about 66%, 80%, 87%, and 97%, respectively, of the analyzer values.

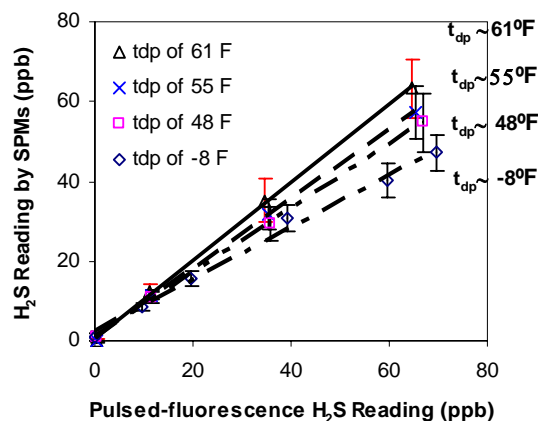


Figure 2. Comparison of H_2S measurements by SPMs (43 units) and a pulsed-fluorescence analyzer for the selected gas concentrations at dew-point temperature (t_{dp}) of -8°F , 48°F , 55°F , and 61°F . The vertical bars of the data points represent standard deviations.

Lab Evaluation - Ammonia

The results of using SPMs for NH_3 measurement are shown in table 2. Overall, when using SPM to measure the change in NH_3 concentration under t_{dp} of -8°F (dry air), 48°F , 55°F , or 61°F , the result will be, respectively, 42%, 86%, 102%, and 178% of the analyzer values.

Regression Analysis

For each type of gas, 43 correctional equations were established to correct SPM readings to the analyzer values. The corrected H_2S readings generally showed a linear trend ($R^2 > 0.99$), having a slope close to 1 and an intercept less than 1. In comparison, the corrected NH_3 concentrations had larger variability. Using regression analysis on all SPMs, a general correctional equation was developed to correct H_2S readings by the SPMs.

Field Evaluation

Hydrogen Sulfide. Overall, H_2S readings by SPMs in field were about 70% of those measured by the analyzer. The field result was consistent with the lab test results where the SPMs displayed approximately 66% and 80% of the analyzer readings when the sample air has a t_{dp} of -8°F and 48°F , respectively. Readings by the SPMs were corrected using either the individually correctional equations or the overall correctional equation derived from the laboratory evaluation. The results were compared with the analyzer readings and linear equations were established. The individually corrected readings

ranged from 0.89 to 1.13 (mean of 0.995, $R^2 = 0.95$) of the analyzer readings, whereas the overall corrected readings ranged from 0.90 to 1.07 (mean of 0.973, $R^2 = 0.95$) of the analyzer readings. Hence, the results showed that H_2S readings by SPMs can be corrected with the overall correctional equation derived from lab evaluation to achieve 90% to 107% agreement with the analyzer readings.

Ammonia. During the first field test at the poultry facility (concentrations between 3.4 and 5.4 ppm, t_{dp} range of 39-45 °F), as-is NH_3 readings of the SPMs were higher than the analyzer readings. Corrected NH_3 concentrations from five units were not significantly different from the analyzer readings ($P > 0.05$). Ammonia concentrations between 7 and 23 ppm (t_{dp} range of 47-63 °F) collected at swine facility (as-is readings) tended to overestimate NH_3 concentration. However, application of the derived correctional equations over-corrected the readings, thereby resulting in significantly lower corrected readings (slopes of 0.59 to 0.90).

SPM NH_3 readings at lower concentrations and low t_{dp} at the poultry facility were improved after correction with the regression equations. However, this was not the case with SPM NH_3 readings at higher concentrations and higher t_{dp} conditions at the swine facility. It was unknown whether the gas samples from the swine building caused interference with the NH_3 measurement, or the SPM chemcassette tape partially lost sensitivity due to aging.

Stability Evaluation

The SPMs showed good stability over 8-month testing period. Changes of SPM readings for H_2S gas between 10 and 70 ppb were less than 12%. Relatively larger change at zero level (-77% to 18%) was mainly due to the lower base value.

Acknowledgements

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Table 1. Summary of Single Point Monitor (SPM) readings for various calibration H₂S concentrations and dew-point temperature under laboratory conditions (n = 44)

Dew-Point Temperature (°F)	Analyzer Concentration (ppb)	H ₂ S Readings by SPM and Statistics				
		Mean (ppb)	Within Units ^[a]		Among Units	
			S.D.	CV (%)	S.D.	CV (%)
-8	0	0.97	0.99	101	0.74	76.3
	9.5	8.5	0.50	5.8	1.03	12.1
	19.5	15.7	0.62	3.9	1.84	11.7
	39.3	30.8	0.81	2.6	3.21	10.4
	59.6	40.3	1.76	4.4	4.24	10.5
	69.9	47.2	1.47	3.1	4.38	9.3
48	0.04	1.1	0.17	15.9	1.34	125
	11.6	11.0	0.36	3.3	1.49	13.6
	35.9	29.5	0.91	3.1	4.22	14.3
	66.8	54.8	1.69	3.1	7.25	13.2
55	0.04	0	0	N/A	0	N/A
	11.5	11.6	0.37	3.2	1.35	11.7
	35.2	31.6	0.91	2.9	3.78	12.0
	65.3	57.3	1.59	2.8	6.76	11.8
61	0.04	0.12	0.21	177	0.26	214
	11.3	12.5	0.52	4.2	1.77	14.2
	34.8	35.2	1.11	3.2	5.42	15.4
	64.7	63.2	2.0	3.2	7.34	11.6

^[a] S.D. = standard deviation; CV = coefficient of variation.

Table 2. Summary of Single Point Monitor (SPM) readings for various calibration NH₃ concentrations and dew-point temperature under laboratory conditions (n = 44)

Dew-Point Temperature (°F)	Reference Concentration (ppm)	NH ₃ Readings by SPM and Statistics				
		Mean (ppm)	Within Units ^[a]		Among Units	
			S.D.	CV (%)	S.D.	CV (%)
-8	0.03	3.0	0.08	2.7	0.24	8.2
	5.2	5.7	0.13	2.2	0.48	8.4
	10.9	8.3	0.21	2.6	0.70	8.4
	16.5	11.1	0.46	4.1	0.92	8.3
	21.5	12.4	0.29	2.3	0.83	6.7
	25.8	13.8	0.40	2.9	0.72	5.3
47-50	0	0.02	0	0	0.06	396
	5.5	8.3	0.33	4.0	1.52	18.3
	13.8	15.8	1.22	7.7	1.47	9.3
	23.7	20.8	1.59	7.6	2.72	13.1
55-57	-0.02	0.01	0	6.8	0.07	958
	5.7	12.3	0.50	4.1	2.10	17.1
	13.8	21.7	1.00	4.6	2.86	13.2
	23.3	24.4	1.15	4.7	2.30	9.4
61-63	0.03	0.09	0.02	22.9	0.42	453
	5.5	14.7	0.66	4.5	2.47	16.8
	9.5	22.0	1.00	4.6	3.53	16.1
	13.6	23.8	1.08	4.5	5.91	24.9

^[a] S.D. = standard deviation; CV = coefficient of variance.